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(54) **A process for production of ethylene and propylene by catalytic pyrolysis of heavy hydrocarbons**

(57) A catalytic pyrolysis process for production of ethylene and propylene from heavy hydrocarbons, comprises that heavy hydrocarbons are contacted with a pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil contained catalysts in a riser or downflow transfer line re-

actor in the presence of steam and catalytically pyrolysed at a temperature of 650°C to 750°C and a pressure of 0.15 to 0.4MPa for a contact time of 0.2 to 5 seconds, a weight ratio of catalyst to feedstock of 15:1 to 40:1 and a weight ratio of steam to feedstock of 0.3:1 to 1:1. The yields of ethylene and propylene by the present invention are over 18wt%.

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Description**Field of the Invention**

5 [0001] The present invention relates to a catalytic pyrolysis process of heavy hydrocarbons, and more particularly to a process for producing light olefins, especially ethylene and propylene, by catalytic pyrolysis of heavy hydrocarbons using catalyst in the presence of steam.

Description of the Prior Art

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[0002] The conventional ethylene production technology is the known tubular furnace steam cracking, which requires light hydrocarbons as feedstock, such as ethane, propane, butane, naphtha or light gas oil.

15 [0003] As the crude oils are becoming heavier, and the supply of light hydrocarbons is limited, great attention has been paid to developing new technologies for directly converting heavy hydrocarbons into ethylene. For example, heavy hydrocarbon thermal cracking using coke particles or quartz as heat carrier, heavy hydrocarbon thermo-catalytic cracking using alkaline metal oxides or alkaline-earth metal oxides as catalyst, etc.. These methods all need reaction temperatures higher than 800°C.

20 [0004] Recently, some methods using solid acidic catalysts in certain types of reactors under certain operating conditions for converting heavy hydrocarbons to light olefins have been introduced and reported in various patents. For example, DD 152,356A discloses a method for producing light olefins using amorphous aluminosilicate catalyst and a fixed or moving bed reactor, when using VGO as feedstock, 13.5wt% ethylene and 6.3wt% propylene are obtained under the reaction temperature of 700°C and the steam to feedstock weight ratio of 4.7. JP 60-222,428 discloses a process using ZSM-5 zeolite as active component of the catalyst and C₅-C₂₅ paraffin hydrocarbons as feedstock, the total yield of ethylene, propylene and butene reaches about 30wt% at a temperature of 600°C to 750°C and a weight hourly space velocity of 20 to 300 h⁻¹. USP 4980053 discloses a process for production of propylene and butene in a fluidized or moving bed reactor using solid acidic catalyst at a temperature of 500°C to 650°C, with a weight hourly space velocity of 0.2 to 20 h⁻¹ and the catalyst to feedstock weight ratio of 2:1 to 12:1, 5.9wt% ethylene, 21.9wt% propylene and 15.6wt% butylene are obtained at a reaction temperature of 580°C using VGO as feedstock and a catalyst with ZSM-5 zeolite as active component and kaolin as matrix. CN1069016A discloses a process for the production of C₂= as well as C₃= and C₄= by converting heavy hydrocarbons in a fluidized bed or piston flow reactor under the main reaction conditions: at a temperature of 650-900°C, a pressure of 0.13-0.28 MPa, a catalyst/oil ratio of 5-35, a contact time of 0.1-3 sec., the yield of C₂= reaches 17-27 wt%, with the total yield of C₂=-C₄= up to 30-40 wt%.

30 [0005] In CN1083092A, molecular sieve catalyst containing a pillared interlayered clay and/or a high silica zeolite catalyst containing rare earth are/is used for cracking heavy hydrocarbons under the conditions of at 680-780°C, 1.5-4.0 × Mpa, a reaction time of 0.1-3.0 sec., with a water/oil ratio of 0.2- 2.0, and a catalyst/oil ratio of 5-40, a yield of 23 wt % C₂= is obtained, with the yield of C₂=-C₄= being 50 Wt%.

Objects of the Invention

40 [0006] The object of the present invention is to provide a novel process for producing light olefins, especially ethylene and propylene, from heavy hydrocarbons in a riser or downflow transfer line reactor. Other objects of the present invention can be learned from the content of the specification of the present invention including the claims.

[0007] The object of the present invention is achieved by the technical solution described below.

45 **Summary of the Invention**

50 [0008] In the process of the present invention, heavy hydrocarbons are contacted with hot pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite flaying a structure of pentasil containing catalysts in a riser or downflow transfer line reactor and catalytically pyrolysed under given operating conditions. The reaction effluent, steam and spent catalyst are separated by rapid gas-solid separation system, the reaction effluent is further separated to obtain ethylene and propylene containing gaseous products and liquid products, and the spent catalyst is further removed to stripper. After stripped by steam, the spent catalyst is removed to a regenerator where it is contacted with an oxygen containing gas and is regenerated, the hot regenerated catalyst is stripped and then recycled to the reactor for reuse.

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Detailed Description of the Invention

[0009] The process provided by the present invention comprises the following steps: the preheated heavy hydrocar-

bons are contacted with hot pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil containing catalysts in a riser or downflow transfer line reactor and catalytically pyrolysed at a temperature of 650°C to 750°C and a pressure of 0.15 to 0.4MPa, for a contact time of 0.2 to 5 seconds, a weight ratio of catalyst to feedstock of 15:1 to 40:1 and, a weight ratio of steam to feedstock of 0.3:1 to 1:1. The reaction effluent, steam and spent catalyst are separated by rapid gas-solid separation system, the reaction effluent removed from the reactor is quenched by light hydrocarbons and further separated to obtain ethylene and propylene containing gaseous products and liquid products, and the spent catalyst is further removed to the stripper. After stripped by steam, hydrocarbon products adsorbed on the catalyst are stripped out. The spent catalyst with coke deposited thereon is then removed to a regenerator, in which the regeneration is carried out by contacting the catalyst with hot oxygen-containing gas, such as air for coke burning off. The regenerated catalyst is stripped by steam and/or other inert gases, to desorb the carried non-hydrocarbon impurities, and then recycled to the reactor for reuse. The hot regenerated catalyst provides the reaction heat for catalytic pyrolysis of heavy hydrocarbons, whereas the heat released by the spent catalyst under regeneration in the regenerator is absorbed by the regenerated catalyst which, when recycling back to the reactor, provides the heavy hydrocarbon feedstocks with the absorbed heat for carrying on the catalytic pyrolysis reaction.

[0010] The catalyst used in the process of the present invention comprises 1~70% by weight of clay, 5~85% by weight of inorganic oxides and 10~70% by weight of active component, wherein said clay is selected from kaolin and/or kaolin polyhydrate, said inorganic oxide is selected from amorphous aluminosilicate, silica or alumina, said active component is selected from pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil.

[0011] One of the active components used in the present invention is pillared interlayered clay molecular sieve, which is aluminum pillared natural or synthetic clay material with regularly interstratified or monostatified mineral clay structure using aluminum containing chemical component as pillaring agent, a quite good one among them is aluminum pillared interlayered rectorite or aluminum pillared interlayered montmorillonite, the preferable one is aluminum pillared interlayered rectorite. The structural characteristics of the rectorite and the preparations of aluminum pillared interlayered rectorite and aluminum pillared interlayered rectorite containing catalysts can be referred to prior art, for example, USP4757040.

[0012] Another active components used in the present invention is phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil, which is a 2~8wt% phosphorus and 0.3~3.0wt% aluminum or magnesium or calcium (based on zeolite weight, calculated as oxides) contained high silica zeolite having the structure of ZSM-5, ZSM-8 or ZSM-11 with optimum Si/Al mole ratio of 15~60. The above said high silica zeolite having a structure of pentasil can be prepared by various known technologies disclosed in prior art, however, a preferable preparing method is as follows: using water glass, aluminum phosphate and inorganic acid as raw materials, and Y zeolite as crystalline seeds, crystallizing at 130~220°C for 12~60 hours. The detailed preparation procedure of the method can be referred to as USP 5232675, the only difference is the present crystalline seed uses Y zeolite without rare earth. The phosphorus and aluminum or magnesium or calcium in the modified high silica zeolite having a structure of pentasil can be introduced by mixing the pre-prepared or purchased high silica zeolite having a structure of pentasil homogeneously with aluminum phosphate sol or magnesium phosphate sol or calcium phosphate sol according to a selected proportion, and followed by calcining at 400~600°C for 3~6 hours in the presence of 60~100% steam; it can also be introduced by mixing pre-prepared or purchased high silica zeolite having a structure of pentasil homogeneously with phosphorus and aluminum or magnesium or calcium containing aqueous solution, and followed by impregnating for 0.5~4 hours, drying, and then calcining at 450~650°C for 1~4 hours.

[0013] The above said modified high silica zeolite having a structure of pentasil can also contain 0.3~3wt% nickel (based on zeolite weight, calculated as oxides). The nickel in the modified high silica zeolite having a structure of pentasil is introduced by mixing nickel containing compound homogeneously with pre-prepared or purchased high silica zeolite having a structure of pentasil and phosphorus and aluminum or magnesium or calcium containing aqueous solution, and followed by impregnating for 0.5~4 hours, drying, and then calcining at 450~650°C for 1~4 hours.

[0014] The suitable heavy hydrocarbon feedstocks used in the present invention can be atmospheric gas oil or vacuum gas oil or the mixture thereof, residual oil or crude oil can be also directly processed. The pattern of feed injection into reactor can be single point injection or multi-point injection.

[0015] The advantages of the present invention in comparison with the prior art are as follows:

1. In a comparison with conventional catalytic cracking process, the process provided by the present invention uses pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil containing catalysts with lower hydrogen transfer activity and higher ethylene selectivity, and capability of increasing the reaction temperature, thus increases the yields of light olefins, especially ethylene and propylene.
2. In comparison with prior catalytic conversion processes for producing light olefins, the process provided by the

present invention uses dilute phase transfer line reactor and pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil containing catalysts with higher cracking activity and higher olefin selectivity, thus increases the yields of light olefins, especially ethylene and propylene.

3. The process of the present invention provides the suitable catalysts, reactor type and operating conditions, thus obtains higher yields of light olefins especially ethylene, wherein the yields of ethylene and propylene can be more than 18wt% respectively.

4. The feedstocks used in the process of the present invention possess wide boiling ranges, which can be atmospheric gas oil or vacuum gas oil or the mixture thereof, and can also be residual oil or crude oil.

[0016] The following examples will serve to further illustrate the catalytic pyrolysis process provided by the present invention. However, these examples shall not be construed to limit the scope of the present invention.

[0017] The catalysts used in these examples of the present invention are as follows:

[0018] Catalyst A is prepared according to the method disclosed in USP 4757040. It comprises 50wt% pillared interlayered rectorite, 15wt% phosphorus and magnesium containing high silica zeolite having a structure of pentasil and 30wt% alumina, with the remainder being kaolin.

[0019] Catalyst B is prepared according to the method of conventional FCC catalyst. It comprises of 15wt% phosphorus and calcium containing high silica zeolite having a structure of pentasil and 57wt% amorphous aluminosilicate, with the remainder being kaolin.

[0020] Catalyst C is prepared according to the method of conventional FCC catalyst. It comprises of 15wt% phosphorus and magnesium containing high silica zeolite having a structure of pentasil and 57wt% amorphous aluminosilicate, with the remainder being kaolin.

[0021] Catalyst D is prepared according to the method of conventional FCC catalyst. It comprises 15wt% phosphorus and aluminum containing high silica zeolite having a structure of pentasil and 57wt% amorphous aluminosilicate, with the remainder being kaolin.

[0022] Catalyst E is prepared according to the method of conventional FCC catalyst. It comprises 20wt% phosphorus and magnesium containing high silica zeolite having a structure of pentasil, 3.5wt% REY zeolite and 25wt% alumina, with the remainder being kaolin.

[0023] Catalyst F is prepared according to the method of conventional FCC catalyst. It comprises 20wt% phosphorus, magnesium and nickel containing high silica zeolite having a structure of pentasil and 25wt% alumina, with the remainder being kaolin.

[0024] The high silica zeolite having a structure of pentasil used in the catalysts A, B, C, D, E and F is a ZSM-5 zeolite having a Si/Al mole ratio of 25 made by the Catalyst Factory of Changling Petrochemical Company in Hunan, China.

[0025] The main physico-chemical properties of the Catalysts A, B, C, D, E and F are listed in Table 1.

[0026] The main properties of the feedstocks used in these examples are listed in Table 2.

Table 1

Catalyst	A	B	C	D	E	F
Chemical Composition, wt%						
Al ₂ O ₃	50.5	40.5	40.0	41.5	46.5	45.4
Na ₂ O	1.03	0.05	0.05	0.05	0.05	0.05
Physical Properties						
SA, m ² /g	200	118	113	120	128	123
PV, ml/g	0.16	0.12	0.11	0.13	0.12	0.12
ABD, g/ml	0.89	0.86	0.86	0.86	0.81	0.82
A.I., wt%/h	3.0	1.0	1.0	1.0	2.4	1.6
Particle Size Distribution, wt%						
0-40 micron	-	26.5	27.2	28.2	16.6	18.8
40-80 micron	-	59.8	58.6	58.1	42.0	58.6
>80 micron	-	13.7	14.2	13.7	41.4	22.6

Table 2

Feedstock	AGO	VGO	ATB	Crude oil
Density (20°C), g/ml	0.8184	0.8730	0.8953	0.8576
CCR, wt%	0.01	0.15	4.17	3.75
Hydrogen, wt%	14.00	13.54	12.94	-
Nickel, ppm	-	0.09	4.78	3.36
Vanadium, ppm	-	<0.01	0.08	<0.05
Distillation, °C				
IBP	242	346	299	-
10%	264	411	389	-
30%	278	437	480	-
50%	290	462	-	-
70%	304	489	-	-
90%	323	523	-	-
EP	347	546	-	-

Example 1

[0027] This example illustrates the process provided by the present invention for production of ethylene and propylene by catalytic pyrolysis of heavy hydrocarbons in transfer line reactor.

[0028] The test was carried out in a riser pilot plant with continuous reaction and regeneration operation system using VGO as feedstock with Catalyst C and operated in a single pass operation mode. The feedstock was preheated to about 350°C and injected into the inlet of riser reactor, high temperature steam was injected to the outlet of preheater and the inlet of riser reactor, the weight ratio of steam to feedstock is 0.8:1. The feedstock was contacted with hot catalyst in a riser reactor and catalytically pyrolysed at a riser outlet temperature of 685°C and a pressure of 0.25MPa for a contact time of 2.5 seconds and with a weight ratio of catalyst to feedstock of 25:1. The reaction effluent, steam and the spent catalyst were separated by rapid gas-solid separation system in the outlet of riser reactor, reaction effluent was quenched by hydrocarbon and further separated to obtain gaseous and liquid products, and spent catalyst was further removed to the stripper. After stripped by steam, the spent catalyst was removed to a regenerator where it was contacted with heated air and was regenerated, the regenerated catalyst was stripped by steam to desorb the carried non-hydrocarbon impurities and then recycled to the reactor for reuse. The results of the test are listed in Table 3.

Table 3

Feedstock	VGO
Catalyst	C
Operating Conditions	
Riser outlet temperature, °C	685
Contact time, sec.	2.5
Catalyst/oil ratio	25:1
Steam/oil ratio	0.8:1
Product Yields, wt%	
Cracked gas	66.67
in which, ethylene	22.02
Propylene	20.81
Butylenes	9.51
C ₅ +naphtha	15.65
LCO	6.44
HCO	3.56
Coke	7.68
Light Olefins Yield, wt%	52.34

Example 2

[0029] This example illustrates the process provided by the present invention for production of ethylene and propylene by using various catalysts selected from the present invention.

5 [0030] The tests were carried out in a bench scale fixed-fluidized bed reactor at a temperature of 680°C, with weight ratio of catalyst to feedstock of 15:1, a weight ratio of steam to feedstock of 0.8:1 and a weight hourly space velocity of 10h⁻¹. The results of the tests are listed in Table 4.

10 [0031] From the data of Table 4, it can be seen that catalysts A, B, C, D, E and F all exhibit high ethylene and propylene yields.

Table 4

Catalyst	A	B	C	D	E	F
Product Yields, wt%						
Cracked gas	67.26	68.61	69.70	69.32	73.97	70.48
in which, ethylene	19.50	19.81	20.77	20.41	22.75	22.26
propylene	21.58	22.72	22.47	22.52	25.13	22.66
butylenes	11.37	10.53	10.69	10.61	10.86	10.37
C ₅ +naphtha	15.02	17.84	15.22	15.05	11.25	14.36
LCO	5.74	3.73	5.33	5.16	3.12	3.48
HCO	4.58	2.64	3.65	4.10	3.03	3.40
Coke	7.40	7.18	6.10	6.37	8.63	8.28
Light Olefins Held, wt%	52.45	53.06	53.93	53.54	58.74	55.29

Example 3

[0032] This example illustrates that heavy hydrocarbons with different boiling ranges can be used as feedstocks in the process provided by the present invention.

30 [0033] The tests were carried out in a bench scale fixed bed reactor using different catalysts. The operating condition and the results of the tests are listed in Table 5.

Example 4

35 [0034] This example illustrates that the full range crude oil can be used as feedstock in the process provided by the present invention.

[0035] The test was carried out in a bench scale fixed bed reactor using Catalyst A. The operating conditions and the results of the tests are listed in Table 6.

Table 5

Feedstock	AGO	VGO	ATB
Catalyst	B	C	A
Operating Conditions			
Reaction temperature, °C	750	700	650
Contact time, sec	2	3	5
Catalyst/oil ratio	15:1	15:1	25:1
Steam/oil ratio	0.3:1	0.8:1	1:1
Product Yields, wt%			
Cracked gas	70.85	75.03	62.38
in which, ethylene	18.98	21.09	18.07
propylene	18.69	23.56	19.25
butylenes	10.23	10.47	9.86
C ₅ +liquid	21.08	17.83	28.10
Coke	8.07	7.14	9.52
Light Olefins Held, wt%	47.90	55.12	47.48

Table 6

Feedstock	Crude oil
Catalyst	A
Operating Conditions	
Reaction temperature, °C	700
Contact time, sec	0.2
Catalyst/oil ratio	40:1
Steam/oil ratio	0.5:1
Product Yields, wt%	
Cracked gas	61.92
in which, ethylene	19.35
Propylene	18.02
Butylenes	10.89
C ₅ +liquid	31.02
Coke	7.06
Light Olefins Yield, wt%	48.26

Claims

1. A process for producing ethylene and propylene wherein heavy hydrocarbons are contacted with hot molecular sieve catalyst in a reactor in the presence of steam and catalytically pyrolysed, the reaction effluent, steam and spent catalyst are separated by rapid gas-solid separation system in the outlet of riser reactor, the reaction effluent is quenched and then separated to obtain ethylene and propylene containing gaseous products and liquid products, the spent catalyst is stripped by steam and then removed to a regenerator where it is contacted with an oxygen containing gas and is regenerated by coke burning off, the regenerated catalyst is stripped and then recycled to the reactor for reuse, wherein said heavy hydrocarbons are contacted with hot pillared interlayered clay molecular sieve and/or phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil containing catalyst in a riser or downflow transfer line reactor and catalytic pyrolysed at a temperature of 650°C to 750°C and a pressure of 0.15 to 0.4MPa, for a contact time of 0.2 to 5 seconds, a weight ratio of catalyst to feedstock of 15:1 to 40:1 and a weight ratio of steam to feedstock of 0.3:1 to 1:1.
2. The process according to claim 1, wherein said catalyst can also contain Y type zeolite molecular sieve.
3. The process according to claim 1 or 2, wherein said pillared interlayered clay molecular sieve is pillared interlayered rectorite.
4. The process according to any preceding claim, wherein said phosphorus and aluminum or magnesium or calcium modified high silica zeolite having a structure of pentasil is a 2 to 8wt% phosphorus and 0.3 to 3.0wt% aluminum or magnesium or calcium (based on zeolite weight, calculated as oxides) containing high silica zeolite having a structure of pentasil with a Si/Al mole ratio of 15 to 60.
5. The process according to claim 4, wherein said modified high silica zeolite having a structure of pentasil can also contain 0.3 to 3.0wt% nickel (based on zeolite weight, calculated as oxides).
6. The process according to claim 4 or 5, wherein said modified high silica zeolite having a structure of pentasil is preparable by mixing high silica zeolite having a structure of pentasil homogeneously with aluminum phosphate sol or magnesium phosphate sol or calcium phosphate sol and followed by calcining at 400 to 600°C for 3 to 6 hours in the presence of 60 to 100% steam.
7. The process according to claim 4 or 5, wherein said modified high silica zeolite having a structure of pentasil is preparable by mixing high silica zeolite having a structure of pentasil homogeneously with phosphorus and aluminum or magnesium or calcium containing aqueous solution, and followed by impregnating for 0.5 to 4 hours, drying, calcining at 450 to 650°C for 1 to 4 hours.

8. The process according to claim 5, wherein said nickel in the modified high silica zeolite having a structure of pentasil is introduced by mixing nickel compound homogeneously with high silica zeolite having a structure of pentasil and phosphorus and aluminum or magnesium or calcium containing aqueous solution, and followed by impregnating for 0.5 to 4 hours, drying, calcining at 450 to 650°C for 1 to 4 hours.
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9. The process according to any of claims 4 to 8, wherein said high silica zeolite having a structure of pentasil is one selected from the group of high silica zeolites having a structure of ZSM-5, ZSM-8 or ZSM-11 type.
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10. The process according to any of claims 4 to 9, wherein said high silica zeolite having a structure of pentasil is prepared by using water glass, aluminum phosphate and inorganic acid as raw materials, and Y type zeolite as crystalline seeds, and crystallizing at 130 to 200°C for 12 to 60 hours.
- 15
11. The process according to any preceding claim, wherein said reaction effluent is quenched by injecting light hydrocarbons into the riser outlet as fast coolant.
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12. The process according to any preceding claim, wherein said heavy hydrocarbon feedstocks are atmospheric gas oil or vacuum gas oil or the mixture thereof as well as residual oil or crude oil.
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